PATENT SPECIFICATION (11) 1 564 363

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(21) Application No. 51065/76 (22) Filed 7 Dec. 1976
(31) Convention Application No. 2555262
(32) Filed 9 Dec. 1975 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 10 April 1980
(51) INT CL³ C11B 15/00 A23G 1/00
(52) Index at acceptance
C5C 9B9A 9B9CX 9D
A2B 302 401 BCC BCE

(19)

(54) A METHOD OF ACCELERATING FAT SOLIDIFICATION

(71) We, DYNAMIT NOBEL AKTIENGESELLSCHAFT a German Company of 521 Troisdorf, bez Koln, Postfach 1209, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of accelerating the solidification of melts comprising fats.

Molten fats are often considerably difficult to solidify on cooling, and in many cases will only solidify from the supercooled melt. Although the solidification rate increases with temperature gradient, the formation of undesirable unstable fat modifications is promoted in this way, resulting in numerous, in some cases inexplicable, difficulties. For example, changes occur both in the structure and in the consistency of the fat. In addition undesirable increases in melting point are encountered *inter alia* in the case of suppositories, whilst so-called rings of fat are formed in the case of chocolate. Accordingly, the primary objective of all conventional solidification processes is to obtain as complete a solidification as possible, in the form of so-called crystallisation during solidification, as early as possible during the cooling phase in order *inter alia* to avoid subsequent crystallisation during storage. This careful crystallisation during solidification which, in some cases, takes several hours, seeks to avoid subsequent difficulties and to obtain complete solidification of the fats in stable form.

It may be concluded from the fact that conventionally, solidification is intentionally carried out carefully and slowly, that any shortening of the solidification time is clearly regarded as dangerous and gives rise to storage difficulties and quality deficiencies. It is for this reason that the use of seed crystals or crystallisation accelerators, although having been successful in promoting the crystallisation of numerous chemical substances, has never been seriously considered in the field of fat preparations, especially since solidified or even crystalline fats of a variety of different kinds have proved to be wholly or substantially ineffective as seed crystals.

Various different kinds of apparatus are used in practice for cooling fat melts or molten preparations containing fat to a degree such that fat crystals are formed to an increasing extent and in turn act as crystallisation seeds for those parts of the melt which have not already crystallised. This process is generally known as "tempering" or even as "precrystallisation".

It has now been found that the solidification of fat melts or molten fat-containing preparations can be promoted by the addition of certain crystalline triglycerides.

Accordingly, the present invention provides a method of accelerating the solidification of a melt comprising a fat or a fat-containing preparation, which method comprises dispersing in the melt a crystalline powder-form composition comprising a mono-acid triglyceride and/or a symmetrical triglyceride, each acid residue of the triglycerides being a saturated fatty acid residue having a carbon chain of at least 10 carbon atoms.

It has been found that the common feature of saturated triglycerides used in accordance with the invention is the stable lowest-energy β-form of the fats. This is surprising because this form is not in keeping with the crystal form of the fats and fat-containing preparations to be solidified, most of which generally do not develop the stable form during conventional production. Preferred triglycerides

of this type which are able to crystallise in the β-form have chain lengths of from 10 to 20 carbon atoms and are monoacid triglycerides, i.e. those with three identical fatty acid residues, or symmetrical triglycerides, in which the middle fatty acid residue has a different chain length from the two outer identical fatty acid residues. In addition, mixtures of several monoacid triglycerides with one another or mixtures of one or even several monoacid triglycerides with a symmetrical triglyceride may be used in the composition of the invention.

Although purity does not have to satisfy overstringent requirements, a minimum content of 70% by weight or, better still, 80% by weight of monoacid and/or symmetrical triglycerides in the composition is preferred. In cases where individual monoacid or symmetrical triglycerides are used, they preferably have a purity of 90% by weight, more preferably 95% by weight.

Providing they are chemically uniform substances, the triglyceride compositions are substances with a clearly defined melting point and, in this respect, differ considerably from the usual fats.

In general, additions of from 0.01 to 1% by weight, based on the particular fat melt, are surprisingly adequate and have a considerable solidification-accelerating effect. Quantities as small as these do not affect the required properties of the products.

Smaller additions may be used if the above-mentioned triglycerides are in monocrystalline form. Monocrystalline triglycerides may be obtained in different ways, for example by tempering or crystallisation from solvents. Tempering may be carried out for exemple by alternately keeping the crystals at a temperature very slightly, i.e. 1.5 to 0.5°C, below their measured melting point and then at a temperature approximately 4 to 6°C below that melting point over a total period of from about 2 to 4 hours. As a result of this treatment, virtually all the crystallites are clearly present in the stable β-form, in addition to which development of the crystallites and crystal surfaces is presumably improved.

The same result is obtained by crystallisation from solvents, such as alcohols, especially ethanol, ethers or low boiling petrol fractions.

It is of particular advantage to produce from these microcrystalline substances a finely crystalline, loosened form, even the smallest additions of which have been found to reduce greatly the solidification time of some fat melts. To this end, the number of individual crystallites is increased and the proportion of very small crystallites increased as far as possible by loosening up the crystal agglomerates in a type of grinding operation and obtaining the small crystals required by subsequent sifting, for example with sieves.

This finely crystalline form is a very light crystalline powder which is limey white in appearance and has a larger inner surface than ground particles of normally compact, transparently solidified fats.

Examination under a microscope reveals, for the most part, that this preferred finely crystalline material comprises small individual crystals with well developed crystal surfaces which have not coalesced and which range from 0.5 to 20 μ in size. The majority of the particles range from 2 to 10 μ in size and have the same particle geometry.

Among the preferred triglycerides with a chain length of C_{10} to C_{20}, which contain only or for the most part the natural even-numbered fatty acid residues, some are less active than others. The chain length C_{16} and C_{18} is the most effective and therefore most preferred. Monoacid triglycerides are more active than symmetrical triglycerides, although on the other hand mixtures with large, but by no means exclusive contents of the monoacid and, in addition, symmetrical triglycerides are also extremely effective. For example, tristearin and tripalmitin are very active, as are the symmetrical triglycerides, 1,3-distearoyl-2-palmitoyl glycerol and 1,3-dipalmitoyl-2-stearoyl-glycerol, also mixtures thereof with a predominant content of tripalmitin.

After the triglyceride compositions have been added in accordance with the invention solidification of the fats or fat-containing preparations generally takes place under the conditions maintained during manufacture of the particular products, for example static solidification below the solidification temperature at a stable or decreasing temperature, cooling at a stable or decreasing temperature or even cooling at a stable or decreasing temperature, accompanied by, for example, stirring or kneading.

In addition to considerably accelerating solidification, the method has been found to improve solidification and give storable products. For carrying out the method and also for subsequent solidification, it is important to select conditions for the

particular product under which the added compositions undergo little or no melting or dissolution in the product.

It has been found that, when added under the conditions under which the process is carried out, the above-mentioned triglycerides show very low solubility during hardening of the products and, noticeably, different triglycerides have equally low solubilities.

Since the products melt at different temperatures and since, accordingly, solidification is carried out at different temperatures, it is preferred to choose compositions or solidification accelerators having a melting point which is 20 degrees C or more higher than the solidification temperature of the product.

The known melting points of the β-forms or β-rich forms may be used as a basis for selection, so that tricaprin with a melting point of 29 to 29.8°C and trilamin with a melting point of 43 to 43.7°C are suitable above all for extremely low melting fats, whilst trimyristin with a melting point of 53 to 53.5°C and, above all, tripalmitin with a melting point of 61 to 62.0°C and tristearin with a melting point of 67 to 67.9°C are suitable for higher melting and also for low-melting fats. In this way the solidification accelerators added coexist in the still liquid melt in the form of finely dispersed solid particles. Accordingly, they are able immediately to initiate solidification crystallisation of the fat melt, i.e. at a time at which no fat crystals from the actual melt are as yet present.

Since, irrespective of particle size, each individual triglyceride crystal acts as a seeding centre, the effect of a given addition (quantity by weight) is greater, the smaller the particle size because the number of particles is in an inverse ratio to their size.

In the context of the invention, fats or fat-containing preparations are products which are solid or predominantly solid at room temperature and, as a result of fats and/or fatty oils present in them, have a reluctance towards crystallisation or a delay in solidification which is typical of lipids.

Examples in the field of foodstuffs are chocolate, fatty glazes and toppings, nutrient fats, such as coconut oil and palm oil, baking fats and fat-containing lecithin preparations.

Examples in the medicinal field are fat-containing or fat-coated dragees or suppositories whilst examples in the field of feeds are milk substitutes and fattening fodders.

The shortening of the solidification time produced by the method of the invention can be demonstrated by various methods. In addition to a general test of consistency as a function of time by penetration measurements, the method described as follows provides a good quantitative assessment of the way in which the solidification accelerators in accordance with the invention work.

In this method, the fat melt is initially pretreated under defined conditions (both thermally and also mechanically) and thereafter cooled with strictly uniform stirring to a predetermined solidification temperature in a measuring kneader. Any resistance encountered by the kneading blades in the fat melt to be tested or its preparation is reflected in a reactive force (torque) in the housing of the drive motor which endeavours to rotate in the opposite direction to the motor. This torque is transferred through a lever system to a chart recorder and recorded in the form of a force/time graph (Brabender-Farinograph-Messtrog S 300 N). Thus, it is possible to determine the time taken by a fat melt at the predetermined solidification temperature to assume a defined degree of solidification which is expressed as the increase in torque in the dimension metreponds (mp).

Accordingly, this apparatus, which was developed for another purpose, namely for measuring the consistency and viscosity of baking dough, makes it possible to obtain an expressive and reproducible measurement, hitherto non-existent in practice, after increasing and refining the measuring range of the recorder.

This test method enables the solidification of fat melts to be objectively observed and assessed and, hence, also provides for quantitative evaluation of all the additives which affect the solidification process.

The following Examples illustrate the invention. Examples 1 and 2 refer respectively to Figures 1 and 2 of the accompanying drawings, each Figure being a plot of time v temperature for a variety of cocoa samples.

EXAMPLE 1
(Comparison)

500 g batches of "Ghana", "Arriba", "Trinidad" and "Bahia" cocoas were melted at 55°C (thermostat I, 60 minutes) in an S 300 N measuring kneader

(Brabender), after which the kneader was switched on and the melts stirred for 60 minutes at the same temperature (T I=55°C). The kneader was then switched over from thermostat I to thermostat II which cooled the kneader to a preselected solidification temperature of exactly 28.0°C which was kept constant for the duration of the actual measurement. After a slight increase in the torque at the beginning of the cooling phase, the force-time curve was initially horizontal as a result of cooling. Depending upon the quality of the cocoa masses, and the different solidification properties of the cocoa fat contained therein ("solidifiability"), an initial slight increase in the kneading resistance, indicative of the formaton of the first crystals, was followed by a progressive increase in the kneading resistance, i.e. torque, as soon as massive solidification and consolidation began. The initially readily fluid melt became plastic and solid. Both the solidification profile and the quantitative evaluation of the test results are apparent from the graph in Figure 1, which shows the solidification profile of the above-mentioned cocoa melts under the described test conditions in the absence of a crystallisation accelerator according to the invention.

EXAMPLE 2

When 1% of microcrystalline tristearin in powder form was added to the cocoa melts according to Example 1 immediately after the beginning of the cooling phase (i.e. at time "0" of Figure 2), the cocoa melts solidified much more quickly. The solidification profile of these cocoa melts treated with a solidification accelerator is shown in Figure 2.

The solidification times of the four cocoa melts investigated are compared in Table 1 below, as the outcome of Examples 1 and 2, with the corresponding values of cocoa melts treated with microcrystalline tristearin as crystallisation accelerator. The strength which, under the conditions specified, makes up a torque of 100 mp was taken as reference value for the degree of solidification.

TABLE 1

Cocoa Type	Degree of Solidification DS/28.0°C/D=100 mp Arriba	Trinidad	Ghana	Bahia
K=control test without any addition	115′	125′	155′	190′
B addition of 1% of tristearin	52′	60′	62′	81′
Shortening of solidification time in mins	63′	65′	93′	109′
Shortening of solidification time in %	55%	52%	60%	57%
Shortening of the solidification time to %	45	49	40	43

EXAMPLE 3

400 g of standard commercial-grade cocoa butter was tested for solidification by the method described in Example 1, both with and without 1% of microcrystalline tritearin as crystallisation accelerator. At a cooling temperature of 28.0°C (measuring temperature), there was still no evidence of solidification after 10 hours in the melt without added accelerator, whereas the melt to which the crystallisation accelerator according to the invention had been added had reached a degree of solidification (as hereinbefore defined) of 40 mp after 207 minutes. At 26.0°C, the same cocoa butter solidified in 496 minutes, but with the crystallisation accelerator in only 54 minutes, i.e. in about 10% of the original time.

EXAMPLE 4

The solidification time of 400 g of unhardened standard commercial-grade coconut oil was tested under the test conditions described in Examples 1 and 2. Without the solidification accelerator, the time required to reach a degree of solidification of 20 mp was 43 minutes, shortening to 28 minutes in the presence of a crystallisation accelerator (1% of microcrystalline tristearin).

EXAMPLE 5

A fat consisting almost entirely of glycerol tricaprinate (melting point approximately 20.0°C) was tested for solidification time under the test conditions of Examples 1 to 3. In the absence of crystallisation accelerator, the melt took 172 minutes to reach a degree of solidification of 20 mp, whereas in the presence of tristearin as crystallisation accelerator the solidification time was shortened to 80 minutes.

EXAMPLE 6

A chocolate topping 70—30—40 was treated in accordance with Example 1 and the solidification time determined following the addition of various monoacid triglycerides (ETG) of myristic acid (C_{14}), palmitic acid (C_{16}) and stearic acid (C_{18}). Results are shown in Table 2.

TABLE 2

% by weight	ETG	Solidification time 60 mp/28°C
0	Control	162 minutes
1	ETG-C_{14}	102 minutes
1	ETG-C_{16}	82 minutes
1	ETG-C_{18}	73 minutes

EXAMPLE 7

The chocolate topping of Example 6 was solidified in the measuring apparatus as described in to Example 1 first at 55°C and then at 28.0°C. In the control test (100 mp), solidification occurred after 102 mins.

The C_{18} ETG used as hardening accelerator was used in the finely crystalline, loosened and sifted form of the microcrystalline crystals. An addition of 1% by weight of accelerator produced at solidification time (ST) of 67 minutes, an addition of 0.5% by weight produced an ST of 75 minutes and an addition of 0.25% by weight produced an ST of 87 minutes. An addition of as little as 0.05% by weight of accelerator still produced an ST of 92 minutes.

EXAMPLE 8

0.1%, 0.25%, 0.5% and 1.0% of a microcrystalline mixture of about 80% by weight of 1,3-distearoyl-2-palmitoyl glycerol and 1,3-dipalmitoyl-2-stearoyl-glycerol and about 20% by weight of tristearin and tripalmitin, were added to 500 g batches of melted chocolate topping 70—30—44 under the conditions of Example 1 immediately at the beginning of the cooling phase (at 28.0°C). The measured solidification times based on a degree of solidification of 100 mp, are shown in Table 3 which also includes for comparison, solidification time of the untreated topping milk.

	No addition	Quantities of mixture added			
		0.1	0.25	0.5	1.0% by weight
$ST_{100\ mp}$/28.0°C	119 minutes	106 mins.	98 mins.	93 mins.	90 mins.

WHAT WE CLAIM IS:—

1. A method of accelerating the solidification of a melt comprising a fat or a fat-containing preparation, which method comprises dispersing in the melt a crystalline powder-form composition comprising a monoacid triglyceride and/or a symmetrical triglyceride, each acid residue of the triglycerides being a saturated fatty acid residue having a carbon chain of at least 10 carbon atoms.

2. A method according to claim 1, wherein the or each triglyceride has a crystal structure in the form of a β-modification.

3. A method according to claim 1 or 2, wherein the or each triglyceride is monocrystalline.

4. A method according to claim 1, 2 or 3, wherein the crystalline powder has a particle size of from 0.5 to 20 μ.

5. A method according to claim 4, wherein the crystalline powder has a particle size of from 2 to 10 μ.

6. A method according to any one of the preceding claims, wherein from 0.01 to 1% by weight of the composition is dispersed in the melt, based on the weight of melt.

7. A method according to any one of the preceding claims, wherein each acid

residue of the or each triglyceride is a saturated fatty acid residue having a carbon chain of from 10 to 20 carbon atoms.

8. A method according to claim 7, wherein the carbon chain has from 16 to 18 carbon atoms.

9. A method according to any one of the preceding claims wherein the mono-acid triglyceride is tristearin or palmitin.

10. A method according to any one of the preceding claims wherein the symmetrical triglyceride is 1,3-distearoyl-2-palmitoyl glycerol or 1,3-dipalmitoyl-2-stearoyl glycerol.

11. A method according to any one of the preceding claims wherein the triglyceride composition has a melting point which is at least 20 degrees C higher than the solidification temperature of the melt.

12. A method according to any one of the preceding claims, wherein the composition is dispersed in the melt before solidification crystallisation.

13. A method according to any one of claims 1 to 11, wherein the composition is dispersed in the melt during or immediately before the solidification by cooling.

14. A method according to any one of the preceding claims, wherein the composition is dispersed in the melt and solidification or tempering takes place at the appropriate temperature.

15. A method according to claim 1 substantially as described in any one of Examples 2 to 8.

16. A method according to claim 1 substantially as described with reference to Figure 2 of the accompanying drawings.

17. A fat or fat-containing preparation whenever solidified from the melt by the method according to any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

SOLIDIFICATION BEHAVIOUR OF COCOAS

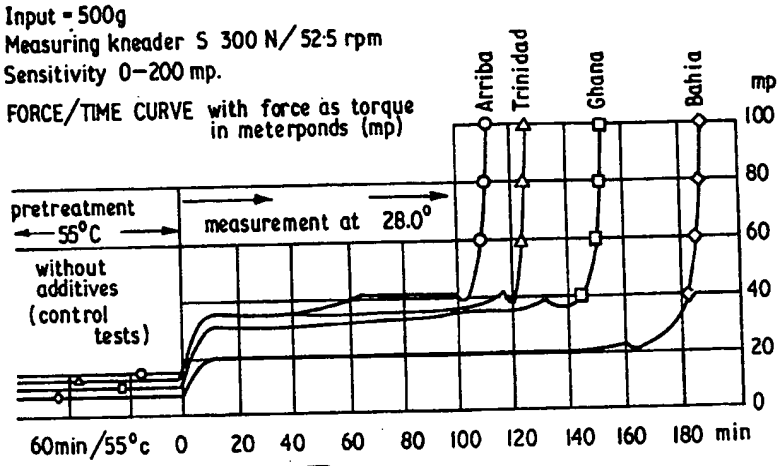

Fig.1.

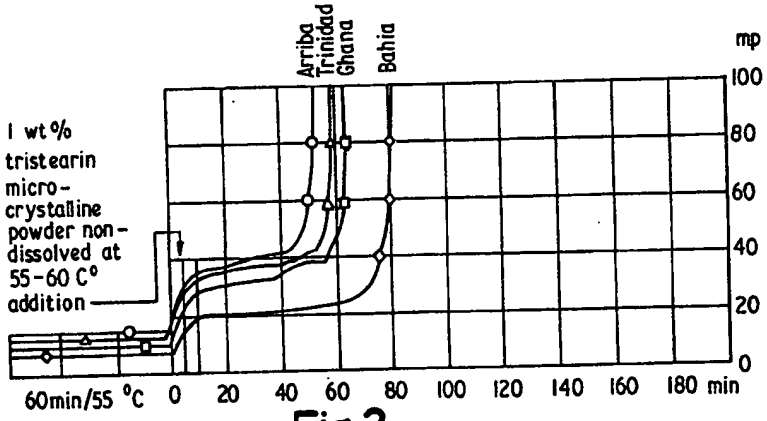

Fig.2.